

REACTION OF DEUTERIUM-LABELED 1,2-DIPHENYLETHANE WITH H_2

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INTRODUCTION

In a previous report, we described experiments carried out in a glass reactor in which 1,2-diphenylethane, DPE, was observed to react with D_2 at 450 °C to give extensive deuterium incorporation in both starting DPE and reaction products.¹ Examination of compounds present by 1H and 2H NMR showed the presence of deuterium in both aliphatic and aromatic positions with somewhat more aromatic D than aliphatic D. Toluene and recovered DPE contained similar amounts of D, 10 - 20% of one atom of D per molecule at low conversions of DPE but increasing with increasing conversion. Certain products, benzene, ethylbenzene, and 1,1-diphenylethane, contained initially higher amounts of deuterium, 50% of one atom or greater, signalling distinct mechanistic pathways.

It was thus suggested that benzyl radicals formed through homolysis of the 1,2-bond in DPE react mainly with unconverted DPE to give toluene and 1,2-diphenylethyl radicals, accounting for the fact that 80% of the initially formed toluene contained no deuterium. The 1,2-diphenylethyl radicals produced were implicated in the removal of D atoms from D_2 . Recently we have shown that 1,2-diphenylethyl radicals generated by an alternate path at lower temperatures are, indeed, capable of promoting reaction with D_2 .² Our earlier work also supported the suggestion of Vernon³ that H atoms produced through the reaction of radicals with H_2 are responsible for the hydrocracking of DPE to give benzene and 2-phenylethyl radicals in that the reaction under D_2 gave ethylbenzene with a relatively high D content in the methyl group and D-enriched benzene.

Because the literature contains abundant evidence that exchange of hydrogens is facile between benzylic positions,⁴ we undertook to determine the extent to which transfer of deuterium between various positions in DPE might complicate our mechanistic conclusions. To this end we have carried out experiments with DPE-1,1- d_2 (two aliphatic hydrogens replaced) and DPE- d_{10} (aromatic hydrogens replaced). The results force modification of our earlier scheme and lead to important new insights.

RESULTS AND DISCUSSION

1,2-Diphenylethane-1,1- d_2 , DPE- d_2 . This compound was prepared as described in the Experimental Section. Tables I and II present data obtained by GC/MS on recovered diphenylethane and product toluene from the thermolysis of DPE- d_2 at 450 °C under N_2 and under H_2 . As will be

noted, at short time periods, listed at < 5 min, 96 to 98% of all diphenylethane molecules contain two atoms of D. This is essentially identical to the composition of starting material. The two D atoms in this material and in the starting material are shown to be positioned on the same atom by the mass spectral fragmentation pattern which shows fragments at m/z of 91 and 93 with very little spectral intensity at $m/z = 92$. After 10 or 15 min at 450 °C, redistribution is evident both under H_2 and under N_2 . It is also apparent that the distribution of D atoms does not change significantly with additional heating (30 min). This indicates that equilibrium is reached after roughly 10 min at 450 °C. Significantly, none of the mass spectra show molecular ions containing more than four atoms of D as would be the case if exchange included the aromatic positions.

One experiment was also carried out with a mixture of toluene-1,1,1- d_3 and DPE- d_0 for 20 min at 450 °C under H_2 . Deuterium transfer to DPE was observed, but this was not extensive, indicating that toluene is a less active partner in the exchange process than is DPE. This is expected based on the relative stabilities of benzyl radicals and 1,2-diphenylethyl radicals.

The non involvement of the aromatic hydrogens was confirmed by NMR measurements combining 1H and 2H NMR in the manner described in our earlier report. These data, shown in Table III, show a small amount of D transfer to the aromatic ring positions under N_2 . Aromatic D in the H_2 experiments is too small to detect. NMR experiments on toluene produced showed no significant aromatic D, however, detection limits for toluene were higher because of small sample size. NMR determination of aliphatic D in toluene gave results in agreement with those obtained by MS.

Importantly, it was also observed that the benzene produced in the H_2 runs contained no significant amount of D by MS measurement. The benzene produced in the N_2 runs, albeit formed in very small amount, showed about 25% of one atom of D per molecule. This suggests that a mechanism exists for the expulsion of D atoms from the benzylic positions but that they react with the aromatic ring only in the absence of H_2 . This clearly indicates that the reaction $D \cdot + H_2 \rightarrow H \cdot + HD$ is rapid under the reaction conditions.

Comparison of the runs carried out under H_2 shows that there is a gradual removal of D from DPE molecules such that approximately half of the original D content of the starting DPE is lost after 30 min at 450 °C. This process is partly due to the reaction of benzyl or 1,2-diphenylethyl radicals with H_2 to add H atoms to the mixture of starting materials and products. This dilutes the aliphatic D present in diphenylethane after its hydrogens are mixed with other aliphatic hydrogens, presumably including those of toluene. However, this is not the entire story because there appears to be a net loss of D from the system and this can also be explained by the expulsion of D atoms from the 1,2 diphenylethylradical as discussed above.

The reaction described above was carried out at a lower temperature to allow observation of the exchange process with greater precision. The results are presented in Tables IV and V. In Table IV it is clear that the exchange of D atoms between DPE molecules is proceeding, but even after 40 min is some distance from the equilibrium situation reached in Table I. It will be noted that in recovered DPE, d_1 molecules accumulate more rapidly than do d_3 molecules despite the fact that at equilibrium (Table I - N_2) they become equal. As the formation of DPE- d_1 involves removal of D and replacement with H

whereas DPE-d₃ requires removal of H and replacement by D, the observed distribution suggests a larger isotopic preference in the replacement process. It is not obvious why this should be so, but the situation is complicated because isotope effects on two reactions are involved.

The deuterium content of the toluene produced from DPE-1,1-d₂ at 420 °C, presented in Table V, is particularly interesting. The total of d₀ plus d₁ toluene molecules is nearly equal to that of d₂ plus d₃, indicating that roughly half of the toluene arises from d₂ benzyl radicals and half from d₀ benzyl radicals. It is also clear that each of these radicals pick up H atoms in preference to D atoms. At least in the experiment carried out under N₂, the only source of hydrogen would appear to be the DPE molecules themselves. Thus it would appear that there is a average isotope effect for the removal of H from DPE by benzyl radicals of roughly $k_H/k_D = 4.6$. It is curious that benzyl-d₂ radicals and benzyl-d₀ appear to be showing somewhat different isotope effects, but this could be an artifact of the analysis of the mass spectral data which is complicated in the case of toluene by facile fragmentation. Also, at longer times, significant scrambling within the DPE occurs prior to conversion to toluene. Nevertheless, the observed isotope effect is almost certainly real and is consistent with studies by Bockrath who found values of 6.5 to 8.0 for the reaction of benzyl radical with a variety hydrogen atom donors at 170 °C in solution.⁵ Comparing the H₂ and N₂ data for toluene shows that there is slightly more D in the toluene from the N₂ runs, but it is not clear whether this comes from H₂ or whether it simply reflects the loss of D from DPE. We are attempting to analyze this situation in greater detail. It seems clear that the major source of H atoms in the toluene formed is the DPE molecule and, at most, about 10 % comes from H₂.

1,2-Di(phenyl-d₅)ethane. This compound was prepared by reaction of 2-phenylethyl chloride with benzene-d₆ and AlCl₃. As it turned out, aromatic exchange with reaction-generated DCl is quite facile giving 1,2-diphenylethane with more than 5 D atoms. By treating the product with more benzene-d₆, AlCl₃ and a trace of D₂O we were able to obtain material which was largely d₁₀. NMR experiments showed no D in aliphatic positions. Preliminary data for the thermolysis of the d₁₀ compound at 450 °C is shown in Table VI. The composition of the diphenylethane recovered after thermolysis under N₂ is essentially that of the synthesized material. The data thus strongly suggest that there is very little transfer of hydrogen from aliphatic to aromatic positions. We presume there is a small amount, based on the experiments with d₂ material, but the present experiment is too insensitive to measure it. Because there is no significant amount of d₁₁ material, it seems probable that there is little or no transfer of D from aromatic to aliphatic positions. This is confirmed by ²H NMR which shows that the amount of aliphatic D is undetectably small in the N₂ experiment (<0.1 atom of D per molecule) and barely measurable in the H₂ experiment (0.15 atom of D per molecule).

These results are particularly important in that they rule out termination steps involving aromatic H-atom adducts. In our previous analysis of the overall process for the thermolysis of diphenylethane under D₂,¹ we suggested a scheme in which H- or D-atom adducts transferred H or D atoms to the various benzylic radicals in termination steps. The experiments with d₁₀ material rule out any significant contribution from such processes. This leaves us without termination steps for the sequence. As it is clear that long chains are not involved (D incorporation does not greatly exceed the amount of conversion to products in D₂ reactions) we need to invoke a

different termination process. The evidence of facile disproportionation of 1,2-diphenylethyl radicals shown in the tetraphenylbutane experiments,² suggests that this is the most important termination step in the DPE reactions.

SUMMARY AND CONCLUSIONS

What is now known about the reaction of diphenylethane with hydrogen?

The first and second steps in Figure 1 are well precedented and general accepted. They are also supported by our work in that we have shown that the dominant reaction of benzyl radicals is with unreacted DPE. The generation of H atoms by the reaction of benzylic radicals with H₂ also is accepted and our work suggests that the 1,2-diphenylethyl radical may be the dominant participant in this process as shown in the fourth reaction in Figure 1.

What now happens to the H atom? Clearly it adds to aromatic rings as evidenced by the incorporation of D when D₂ is used. However, the adducts must be too unstable to survive at concentrations high enough to react with either benzyl or diphenylethyl radicals as shown by the experiments with d₁₀ material. Thus when an H atom reacts with an aromatic ring, it simply generates another H atom (or occasionally a 2-phenylethyl radical but this most likely reacts with H₂ to give another H atom). Because the reverse of the fourth reaction is an energetically downhill reaction, it seems likely that most H atoms will simply give back 1,2-diphenylethyl radicals by H-atom extraction from DPE. If, however, stilbene is present, another option presents itself, that of the fifth reaction in Figure 1 which also gives a diphenylethyl radical. With disproportionation of 1,2-diphenylethyl radicals included as shown in the third equation in Figure 1, the third and fifth steps constitute a route for disposal of H atoms. Combining the five processes in Figure 1, in proper proportion totals to a stoichiometrically correct result for the conversion of diphenylethane to toluene.

The mechanism would then work as follows. Benzyl radicals are formed and equilibrate with 1,2-diphenylethyl radicals. This process is clearly demonstrated by scrambling, etc. 1,2-diphenylethyl radicals having no exothermic reaction available other than reversible dimerization to a species which is unstable at 450 °C (tetraphenylbutane) or disproportionation, build to relatively high concentrations and disproportionate. When the occasional H atom is formed, it adds reversibly to aromatic rings, extracts H atoms from benzylic positions and reacts with stilbene formed in the disproportionation. At low substrate concentrations, the reaction of radicals with H₂, present at high concentration is favored and relatively little stilbene accumulates.

If this sequence is correct, it would explain the relatively high amounts of deuterium incorporated in DPE which is formed as a side reaction in the thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane.⁶ We have found that stilbene is formed as a side reaction in thermolysis of this compound. If it is serving as a D-atom scavenger, this would explain not only why DPE enriched in D₂ is found, but also why there is relatively little aromatic D incorporation in other products. Considering that we now know that D-atom adducts of phenyl rings do not build up in these systems, it is reasonable to presume that the reaction of D atoms with phenyl rings is somewhat endothermic. This being the case, stilbene may be an effective scavenger of wandering H

(or D) atoms. We are presently trying to design experiments to demonstrate the role of stilbene.

There are a number of potentially important implications of this analysis. It would, for example, suggest that a role of catalyst in promoting cleavage of Ar-R bonds in coal liquefaction and related model studies could be simply to facilitate hydrogenation of species which might otherwise trap H atoms. In coal, the role of H-atom trap would likely be played by various polynuclear aromatic compounds as well as various reaction-produced elimination products. A paper by Bockrath, Schroeder and Keldsen reports an effect of 9-methylantracene which could be interpreted in this way.⁷ A thorough understanding of this phenomenon might lead to a better design for catalysts. We are excited about the relative simplicity and the potential implications of this model.

EXPERIMENTAL

2-Phenylethanol-1,1-d₂. Methyl phenylacetate (3.5 g, 23.2 mmol) was dissolved in ether to make a ca. 1 M solution and this was added to a 1 M ether solution containing 1 g of LiAlD₄ at 25 °C. This was allowed to stir under N₂ for 30 min. This was treated with a saturated solution of NH₄Cl in water and the ether layer separated. The ether layer was dried with anhydrous Na₂SO₄ and the solvent removed by rotary evaporation. ¹H NMR (CDCl₃) δ 2.85 (s, 2.0 H), 7.2 (m, 5 H). This was used without further purification.

2-Phenylethyl chloride-1,1-d₂. The alcohol prepared above (2.0 g, 16 mmol) was treated with 10 mL SOCl₂ and 4 mL pyridine and the reaction mixture was stirred at 25 °C for 30 min followed by cautious treatment with about 10 mL water. The resultant mixture was extracted with 50 mL ether. The ether was dried and evaporated as above. This was used without purification in the following reaction.

1,2-Diphenylethane-1,1-d₂. The crude chloride prepared above (1.4 g, 9.9 mmol) was dissolved in 10 mL of spectrometric grade benzene and this was added to anhydrous aluminum chloride (1.5 g, 11.3 mmol) at 0 °C. The reaction mixture was stirred for 40 min followed by treatment with water and extraction with ether (ca. 75 mL of each). Drying and removal of ether as before gave crude product. This was purified by column chromatography on silica gel in hexane to give 1.02 g of product mp 48-50 °C, ¹H NMR (CDCl₃) δ 2.91 (s, 2.0 H), 7.2 (m, 10 H). MS gave m/z 184, 93, 91.

1,2-Di(phenyl-d₅)ethane. 2-Phenylethyl chloride (2.0 g, 14.2 mmol) was dissolved in benzene-d₆ (5 g, 58 mmol) and the solution added to aluminum chloride (2.8 g, 22.6 mmol) following the procedure described above. The crude product was redissolved in fresh benzene-d₆ and treated with fresh AlCl₃ and a drop of D₂O. Work-up and purification as described above gave product mp 48-50 °C. ¹H NMR (CDCl₃) δ 2.92 (s), aromatic resonance was less than 5% of the aliphatic resonance. MS gave m/z 192, 96.

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Table I. Composition of 1,2-Diphenylethane after Thermolysis of 1,2-Diphenylethanes-1,1-d₂ at 450 °C.

	d ₀	d ₁	d ₂	d ₃	d ₄
<5 min (H ₂)	1.75	1.49	96.4	0.12	0.15
10 min (H ₂)	26.3	29.8	32.3	11.3	0.4
30 min (H ₂)	29.7	41.7	22.5	5.5	0.6
<5 min (N ₂)	1.6	0.7	97.5	0.1	0.1
15 min (N ₂)	5.6	22.9	46.3	21.7	3.0
30 min (N ₂)	7.8	23.8	42.2	22.4	3.8

Table II. Toluene from Thermolysis of Diphenylethane-1,1-d₂ at 450 °C.

	d ₀	d ₁	d ₂	d ₃
<5 min (H ₂)	44.3	4.8	50.1	0.8
10 min (H ₂)	34.0	32.5	30.1	3.4
30 min (H ₂)	42.1	43.3	13.1	1.5
<5 min (N ₂)	---	---	---	---
15 min (N ₂)	26.2	30.1	35.9	7.8
30 min (N ₂)	25.4	31.9	35.3	7.5

Table III. NMR Analysis of Recovered Diphenylethane from Thermolysis of 1,2-Diphenylethane-1,1-d₂.

Conditions	aliphatic	D atoms/molecule aromatic
H ₂ (10 min)	1.96	<0.09
H ₂ (30 min)	1.19	<0.09
N ₂ (15 min)	1.98	0.09
N ₂ (30 min)	1.84	0.16

Table IV. Composition of 1,2-Diphenylethane after Thermolysis of 1,2-Diphenylethane-1,1-d₂ at 420 °C.

	d ₀	d ₁	d ₂	d ₃	d ₄
10 min (H ₂)	0.4	12.0	86.0	1.5	0.17
20 min (H ₂)	2.3	19.6	73.6	4.2	0.18
40 min (H ₂)	5.9	29.5	59.5	5.0	0.20
10 min (N ₂)	1.6	4.8	91.6	2.0	0.1
20 min (N ₂)	1.6	11.1	83.1	4.0	0.1
40 min (N ₂)	2.9	16.5	71.6	8.7	0.3

Table V. Toluene from Thermolysis of Diphenylethane-1,1-d₂ at 420 °C.

	d ₀	d ₁	d ₂	d ₃
10 min (H ₂)	42.8	7.6	46.7	3.0
20 min (H ₂)	40.3	12.4	42.8	4.5
40 min (H ₂)	41.2	16.3	39.4	3.0
10 min (N ₂)	37.3	10.9	45.0	6.7
20 min (N ₂)	37.1	13.2	41.9	7.8
40 min (N ₂)	33.5	17.1	39.6	9.8

Table VI. Thermolysis of 1,2-Di(phenyl- d_5)ethane (DPE) at 450° C (20 min).

Composition	Reaction under N_2		Reaction under H_2	
	DPE %	Toluene %	DPE %	Toluene %
d_{10}	55	--	2	--
d_9	22	--	8.5	--
d_8	8	--	17.4	--
d_7	3.2	--	22.3	--
d_6	2.6	--	20.2	--
d_5	2.2	59	13.2	11.4
d_4	--	32	7.0	31.8
d_3	--	9	3.6	33.8
d_2	--	--	2.4	13.8
d_1	--	--	1.8	6.8
d_0	--	--	1.5	2.4

